Spring 1963

A Kinetic Study of the Deiodination of N, N-Dimethyl-P-Iodoaniline

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A KINETIC STUDY

of

THE DEIODINATION OF N, N-DIMETHYL-p-IODOANILINE

A Thesis Presented to the Graduate Faculty

of the Fort Hays Kansas State College in

Partial Fulfillment of the Requirements for

the Degree of Master of Science

by

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ABSTRACT

A KINETIC STUDY ON THE DEIODINATION
OF N, N-DIMETHYL-P-IODOANILINE

A comparative kinetic study was made to determine whether the proposed deiodination mechanism[2] may be extended to include deiodination of N, N-dimethyl-p-iodoaniline in acid medium.

From the kinetic data obtained using classical iodometry, the rate constants and the activation energy of reaction are obtained. At 80°C, the deiodination N, N-dimethyl-p-iodoaniline is faster by a factor of 5 than that of p-iodoaniline. This is explained in terms of chemical structure.

In order to confirm the mechanism, the deuterium effect is measured and interpreted. The ratio, k_{H2O}/k_{D2O}, is found to be 5.8.

Infrared spectra of N, N-dimethyl-p-iodoaniline and N, N-dimethylaniline are given.

The iodine - addition complexes of N, N-dimethyl-p-iodoaniline are described.

ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to Dr. Harold S. Choguill for the suggestion of the problem, arrangement of the new laboratory for this study, and guidance which encouraged the work to completion.

The author also thanks all the staff members of the Chemistry department for their helpful suggestions throughout the research.

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INTRODUCTION

There are many chemical reactions which change the reaction direction by altering their environment. Reactions between iodine and some aromatic amines and phenols have been known to change the reaction direction with unusual ease compared with similar reactions involving other aromatic halides.

Soon after the development of kinetic methodology to interpret the mechanistic pictures of organic reactions, rate of the forward reaction of the aromatic iodination of aniline was investigated and its mechanism was interpreted.[1] For the reverse reaction, however, there had been no kinetic investigation until Choguill and Ridd[2] published their results of research on the deiodination of p-iodoaniline following Gold and Whittaker's study of deiodination of p-iodophenol.[3]

Choguill and Ridd[2] suggested that the deiodination of p-iodoaniline in acidic media is a S_E2 electrophilic substitution, with the iodine-scission step as the rate determining step. This mechanistic picture was supported recently by Choi[4] in his research on the case of o-iodoaniline.

Following the above investigations, this author has been interested in applying the proposed mechanism to the case of N, N-dimethyl-p-iodoaniline and providing further evidence for the mechanism. It has been also intended by the author to interpret the substituent-effect in terms of chemical kinetics and to make

a quantitative comparison of substituted amines* on the basis of their reactivities toward deiodination in acidic media.

The author was interested in obtaining infrared spectroscopic evidence of the course of reaction, but the presentation of evidence in this thesis was not possible as the C - I bond spectrum was outside the range of the spectrophotometer which was available.

The author thinks it is important to mention in this report that there is a remarkable tendency in the reaction mixture of deiodination of N, N-dimethyl-p-iodoaniline to form iodine-addition complexes. A little information on this complex formation is available[5], but it is still ambiguous.

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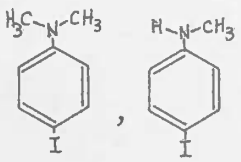
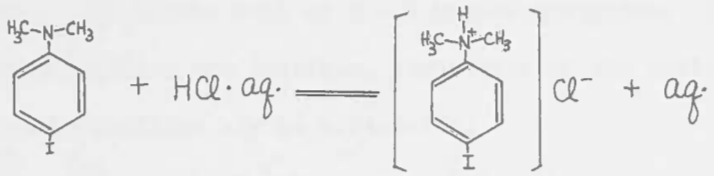
*For instance,  etc.

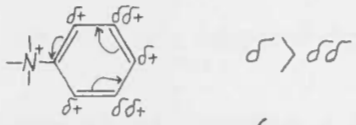
THEORY

I. N, N-Dimethyl-p-iodoaniline in Acidic Medium

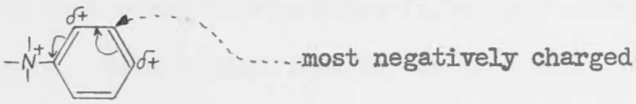
It is well understood that N, N-dimethyl-p-iodoaniline is very slightly soluble in water, but very soluble in acidic solvents, forming its substituted ammonium ion by protolysis.



The $-\overset{+}{N}R_3$ or $-\overset{+}{N}R_2H$ groups are extremely strong electron attractors. They become extremely strong meta-directors toward electrophilic substitutions, creating a relatively great electron density at that site (meta position). Accordingly the para position becomes positive (lower electron density).

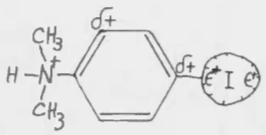


In another expression[6],



This kind of electron distribution can be understood from the conception of chemical resonance.

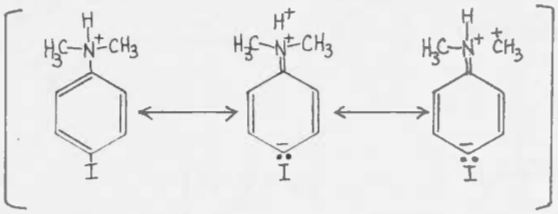
In the case of N, N-dimethyl-p-iodoaniline, the following electron distribution could be postulated:



ε : Intraatomic charge

As shown above, the δ^+ at the para position is neutralized by the intraatomic polarization of highly polarizable iodine atom (the electronegativity of iodine is the same as that of carbon, 2.5 on Pauling's electronegativity scale).

Consideration of contributing structures presents the possibility of N - C hyperconjugation as well as N - H hyperconjugation. If both types of hyperconjugation are possible, structures of the protonated N, N-dimethyl-p-iodoaniline may be postulated.

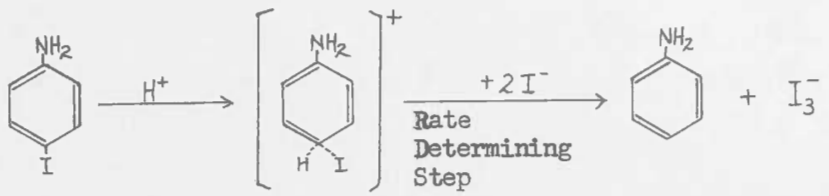


However, there have been no reports of N - C hyperconjugation, so if contribution of N - C hyperconjugation does exist, it will be of small effect, even compared to N - H hyperconjugation.

II. Mechanism of Deiodination of N, N-Dimethyl-p-iodoaniline

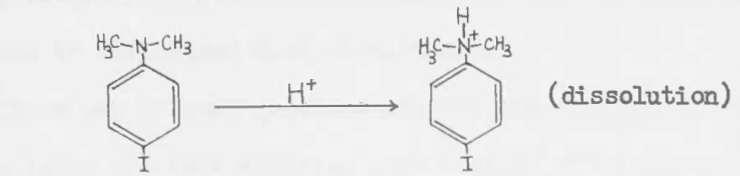
It is well known that an iodoaniline can be deiodinated in acidic media. This is also true in the case of N, N-dimethyl-p-iodoaniline. However, it was not until 1961 that a mechanistic study on the deiodination of p-iodoaniline was first reported.

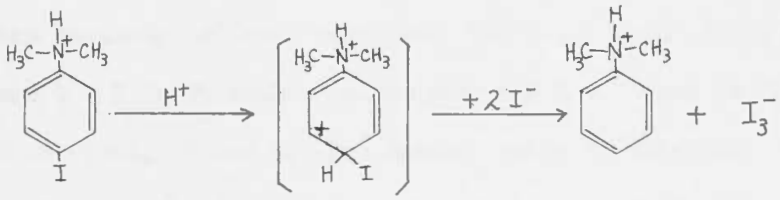
Choguill and Ridd suggested a S_E2 mechanism for deiodination, in which the iodine-scission step of the activated complex is the rate determining step.



The above reaction is essentially a reverse of the iodination of aniline suggested by Berliner[1]. Consequently, the transition state of iodination and deiodination is postulated to have the same structure. Kinetics of iodination and deiodination differ considerably.

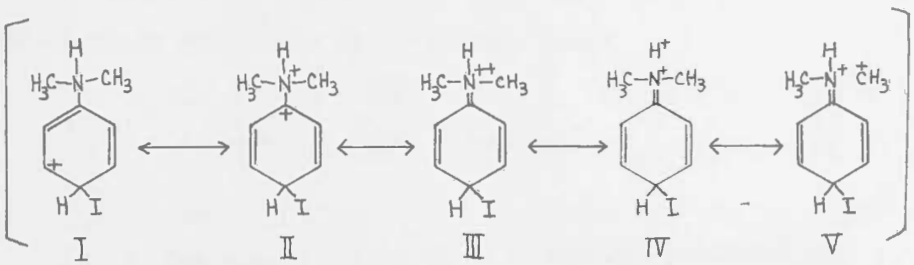
The following analogous mechanistic picture can be proposed for the case of N, N-dimethyl-p-iodoaniline in spite of slightly different molecular structure.





This expected mechanism is to be studied in the present research.

A discussion on the transition state is necessary here to understand the difference between the case of p-iodoaniline and the present case. The transition state, the activated complex, has two positive charges, particularly in the case of N, N-dimethyl-p-iodoaniline and should exhibit the following resonance structures.



Among the above canonical structures, the form I (with a positive charge at meta position) is considered to be most contributive. The structure III with double charges on nitrogen is an extremely high energy form, but it could be possible to stabilize by N - H and N - C hyperconjugation. However, this stabilization by hyperconjugation is difficult to imagine in this case, because it favors decomposition rather than stabilization. The structure I contributes most and is considered most significant.

There may be some question whether the hydrogen or the iodine should leave the para position more easily. This may be answered from the knowledge of bond energies. The C - I bond energy is 56 kcal and C - H is 99 kcal. Accordingly the C - I bond is likely to be broken first. There is also another point to consider; that is, the breakage of the C - I bond is stabilized by the formation of more stable products. In other words, very stable products, N, N-dimethyl-p-iodoaniline and the triiodide ion are formed. However, there is no reason why the breakage of the C - H bond cannot occur, but the probability is negligible compared with that for the C - I breakage.

If we agree with the above reasoning and if the activated complex decomposition is the rate determining step, the kinetic equation of deiodination would have the following form:

$$\text{Rate:} \quad -\frac{d[A]}{dt} = -\frac{d[T]}{dt} = \frac{d[I_3^-]}{dt}$$

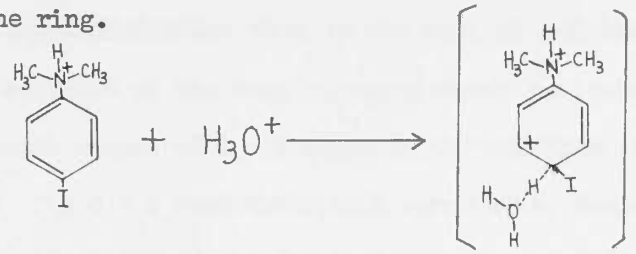
$$= k[A]$$

$[A]$: The concentration of N, N-dimethyl-p-iodoaniline

$[T]$: The concentration of transition complex

$[I_3^-]$: The concentration of the triiodide ion formed.

There is still another problem to consider; the mode of proton attack on the carbon atom bonded to iodine. A hydrogen ion, a proton, exists as a solvated form, a hydronium ion, in aqueous acidic medium, and so the hydronium ion rather than a bare proton attacks the carbon atom of the ring.



Accordingly the transition complex is hydrated. This postutate leads us to the iodine-scission process in which the hydrogen bond (O •• H) breakage occurs at the same time. This reasoning may be verified by the deuterium isotope effect measurement.

If the rate of deiodination is determined by the proton transfer from the hydronium ion, kinetic isotope effect should result in a slower rate of deiodination using deuterium oxide as a medium than using water as a medium. Some investigations suggested that the primary isotope may decrease the rate by factor of 4 or greater. In addition, the change to a deuterated medium should lower the free amine concentration.[7]

III. Effect of Substituents

If there is a difference between the deiodination rates of p-iodoaniline and N, N-dimethyl-p-iodoaniline, it should be explained on the basis of the stability of the transition state and also the stability of the products.

If the activation energy of the deiodination of N, N-dimethyl-

p-iodoaniline is smaller than that of p-iodoaniline, the deiodination of N, N-dimethyl-p-iodoaniline should go faster. The smaller activation energy also means that the C - I bond of N, N-dimethyl-p-iodoaniline is weaker than that of p-iodoaniline, and the situation is more favorable for deiodination than in the case of p-iodoaniline.

This argument on the bond strength should be tested by comparing the absorption ranges of C - I bonds on the infrared spectra of two compounds. The C - I bond absorption range of N, N-dimethyl-p-iodoaniline should be shifted toward the lower energy side if the deiodination of it goes faster.

This difference of C - I bond strength of the compounds discussed above is supposed to be due to the effect of replacement of hydrogen atoms of primary amine by alkyl groups.

No evidence is indicated in chemical literature of a substitution comparable to that of the present investigation. However, it has been shown that, in case of nitration, the replacement of the $-\overset{+}{N}H_3$ group by $-\overset{+}{N}(CH_3)_3$ group decreases the rate of meta-substitution by a factor of 38 and the rate of para-substitution by a factor of about 200.[8]

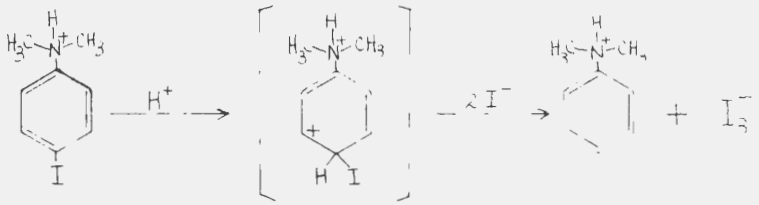
Accordingly, it could be expected that the deiodination of N, N-dimethyl-p-iodoaniline could go faster than that of p-iodoaniline. The possible interpretation of this effect includes the effect of hyperconjugation, hydrogen bonding with solvent and the immobility of $N-CH_3$ group in the transition state. No indication was given of the relative contribution of any one of these effects mentioned.

IV. Experimental Method

Many methods are applicable to kinetic study, depending upon the character and purposes of the kinetic studies. In the present research, the measurement of the rate constants and the determination of the activation energy are the important factors, so that an accurate analytical method is necessary.

There are many analytical methods available for deiodination studies such as optical methods and electrochemical methods. At the same time, the classical titration method should give very complete information.

The kinetic data on the deiodination are obtained by determining the concentration of iodine released.



In this experiment, the classical titration method is applied and the concentration of triiodide ion is determined by titration with standardized thiosulfate solution.

The rate constants are calculated from the kinetic data which are obtained by titrating aliquots of the reaction mixture at programmed time intervals.

The activation energy of the reaction is obtained from the rate constants at different temperatures, using the Arrhenius equation of the activation energy.

EXPERIMENTAL

I. Preparation of N, N-Dimethyl-p-iodoaniline

There are various procedures for the synthesis of N, N-dimethyl-p-iodoaniline. However, the direct method[9] in which N, N-dimethyl-p iodoaniline can be made from N, N-dimethylaniline and elemental iodine in basic medium is the most convenient. This method actually gives a better yield of para product when iodinating N, N-dimethylaniline than it does for aniline itself. Accordingly the author used the following procedure.

In a 1-ℓ. beaker are placed 48 g. of N, N-dimethylaniline, 50 g. of $NaHCO_3$, and 350 ml. of water. The mixture is cooled to 12 – 15° C by adding a small amount of ice. The beaker is then fitted with an efficient mechanical stirrer and the mixture is agitated violently. Eighty-five g. of powdered iodine is then added in 10 - 15 g. portions at 20 or 30 min. intervals, so that it takes about one and one-half hours to introduce all the iodine. Stirring is continued for 20 to 30 min. By this time, the reaction is complete and the color of the free iodine has practically disappeared. The crude product, which separates as a dark mass, is collected on a Büchner funnel, pressed as free from water as possible, and dried in a stream of air.

For the purification of N, N-dimethyl-p-iodoaniline, the desired product is extracted by hot ligroin from the crude mass. The hot ligroin solution is decanted and set in an ice-salt bath to recrystallize the product. Using successive 200 ml. portions of ligroin, this extraction is done three times. The crystalline product forms as practically colorless needles.

In order to further purify the product, the product is recrystallized from ligroin a few more times. In one of those recrystallizations, active charcoal is used to remove the last traces of iodine.

The final product is completely colorless and melts at 82°C. The yield is about 70%, excluding mechanical losses.

II. Kinetic Measurements

Preparation of the Reaction Mixture: The necessary amount of pure N, N-dimethyl-p-iodoaniline is weighed out on an analytical balance and dissolved in a definite amount of standardized hydrochloric acid. In this manner, a predetermined concentration of acid may be obtained in the final reaction mixture. The HCl solution of the sample is transferred to a volumetric flask and diluted to about one eighth of the capacity of the volumetric flask. Then the necessary amount of analytical grade potassium iodide is weighed out and dissolved in the least amount of water. This potassium iodide solution is then transferred into the volumetric flask containing the HCl solution of the sample and then the flask is filled to volume with water, and is ready for the kinetic measurement.

The Kinetic Measurement: The apparatus which was used for the kinetic measurements is diagrammed on page 12 (Fig. 1). A sampling device was incorporated to facilitate removal of aliquots for titration. A thermostat controlled the temperature of the reaction mixture to $\pm$ 0.05° C.

One liter of the reaction mixture is introduced into the reaction flask which has been heated in the thermostat to the reaction temperature.

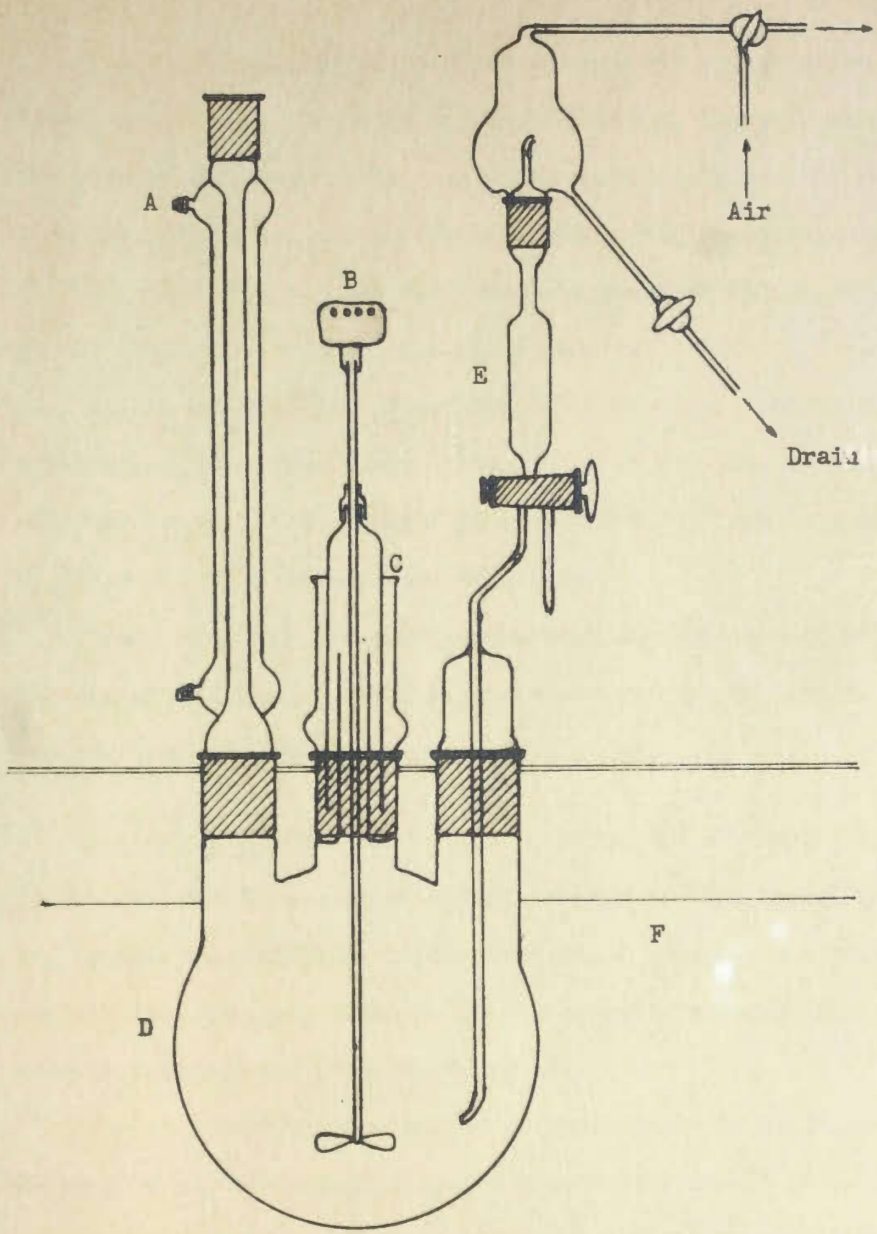


Figure 1. Sampling Device
A. West condenser; B. Stirring motor; C. Mercury seal; D. 1 l.-Three-neck reaction flask; E. 10 ml. automatic pipette; F. Thermostat.

Ten ml. of samples of reaction mixture are withdrawn at programmed intervals of time. In order to prevent further reaction after sampling, the samples are immediately chilled in an ice bath and the iodine is titrated after a certain period of cooling with standardized thiosulfate solution. A 5 ml. microburet is used for the titration of 10 ml. samples. Thyodene is used as the indicator.

As the deiodination progresses, a precipitate appears in the chilled samples. This precipitate, which is presumed to be an iodine-addition complex of N, N-dimethyl-p-iodoaniline,[5] can be decomposed by the addition of thiosulfate solution.

Blank reactions are carried out with the same procedure, using the mixtures without N, N-dimethyl-p-iodoaniline, but otherwise of the same composition as the reaction mixture.

Deuterium Effect: The titration method is not desirable for determination of a deuterium effect because of the limited quantity and expense of deuterium oxide. However, a colorimetric method can replace the titration method. In the present research, the colorimeter used is a Bausch and Lomb Spectronic 20.

The procedure of this series of experiments is as follows. Using a 10 ml. volumetric flask, the necessary amount of N, N-dimethyl-p-iodoaniline is dissolved in a certain amount of D_2O - HCl solution. This D_2O - HCl solution is prepared by mixing the necessary amount of standardized concentrated hydrochloric acid with $4 \sim 5$ ml. of deuterium oxide. The concentrated hydrochloric acid is used to minimize the water (H_2O) contamination. At this time, the preweighed KI is dissolved in $2 \sim 3$ ml. of deuterium oxide and is poured into the

volumetric flask containing the above sample solution. The flask is then filled to volume with deuterium oxide. The reaction mixture is now ready for the kinetic run.

The reaction mixture is introduced into a 10 ml. colorimeter cell with a stopper. This cell is then placed in the thermostat. At the programmed time interval, the cell is removed from the thermostat and placed in the colorimeter which has been previously calibrated, using the same cell. The transmittance of the reaction mixture at 550 mμ is found.

The measurement is carried out as quickly as possible to minimize the temperature drop of the cell. After measurement, the cell is returned to the thermostat.

The blank run is carried out with exactly the same procedure, except without N, N-dimethyl-p-iodoaniline in the sample. A concentration-transmittance curve is obtained by using a series of standardized solutions of iodine in water-HCl solution. This curve is used to convert the transmittance data into concentration data.

Infrared Spectroscopy: As a supporting material for the results of the kinetic study, the infrared spectra can give a good material. However, it is the author's misfortune that the absorption range of the C - I bond is out of the limited range of the common infrared spectrophotometer.

The infrared spectra of N, N-dimethyl-p-iodoaniline were obtained, using carbon tetrachloride or carbon disulfide as solvent in a rock NaCl cell. The infrared spectrum of N, N-dimethylaniline is obtained without any solvent. The infrared spectrophotometer used is Beckman - IR5A.

EXPERIMENTAL DATA AND CALCULATIONS

TABLE I

KINETIC DATA

Time (min.)	Titer[a] (ml.)	(T-B)corr.[b] (ml.)	$n_{(I_2)}$[c] (mole x 10^5)	$n_{(p\text{-DMIA})}$[d] (mole x 10^5)	$\log \frac{n_o}{n_o - X}$[e]
0	0.10	0.10	5.0	995.0	0.0022
5	0.20	0.16	8.0	992.0	0.0035
10	0.30	0.29	14.5	985.5	0.0066
15	0.54	0.43	21.5	978.5	0.0097
20	0.78	0.64	32.0	967.0	0.0145
25	0.92	0.75	37.5	962.5	0.0168
35	1.27	1.04	50.2	949.8	0.0223
45	1.66	1.37	68.5	931.5	0.0311
55	2.06	1.51	75.5	924.5	0.0348
65	2.37	1.98	99.0	910.0	0.0410
80	2.85	2.40	120.0	880.0	0.0554
95	3.34	2.84	142.0	857.0	0.0670
110	3.81	3.27	163.5	836.5	0.0775
125	4.25	3.68	184.0	815.0	0.0888
145	4.86	4.26	213.0	786.0	0.1045
165	5.35	4.74	237.0	763.0	0.1175
185	5.86	5.23	261.5	738.5	0.1319

Note: Reaction temperature: 80 ± 0.05° C. Ten ml. aliquots of the reaction mixture of which initial concentration is 0.01 M N, N-dimethyl-p-iodoaniline, 0.025 M KI, and 0.05 M HCl are titrated with 0.01 N[a] $Na_2S_2O_3$ solution.

a. 0.0100 N $Na_2S_2O_3$ solution is used.

b. Blank correction ((T-B) corr. = Titer - Blank)

c. The number of moles of iodine released

d. The number of moles of N, N-dimethyl-p-iodoaniline reacted

e. n_o: The number of moles of N, N-dimethyl-p-iodoaniline present in the initial reaction mixture

X: The number of moles of N, N-dimethyl-p-iodoaniline reacter (= $n_{(p\text{-DMIA})}$)

TABLE II

KINETIC DATA

Time (min.)	Titer (ml.)	(T-B)corr. (ml.)	$n(I_2)$ (mole x 10^5)	$n_{(p\text{-DMIA})}$ (mole x 10^5)	$\log \frac{n_0}{n_0 - x}$
0	0.050	0.050	2.5	997.5	0.0013
5	0.120	0.080	4.0	996.0	0.0017
10	0.175	0.100	5.0	995.0	0.0022
15	0.230	0.110	5.5	994.0	0.0026
20	0.295	0.140	7.0	993.0	0.0031
25	0.410	0.240	12.0	988.0	0.0052
35	0.570	0.340	17.0	973.0	0.0074
45	0.710	0.420	21.0	979.0	0.0092
55	0.850	0.500	25.0	975.0	0.0100
67	1.000	0.600	30.0	970.0	0.0132
75	1.165	0.730	37.0	963.0	0.0164
95	1.440	0.940	47.0	953.0	0.0209
115	1.700	1.150	58.0	942.0	0.0259
135	1.950	1.360	68.0	932.0	0.0311
155	2.220	1.610	81.0	919.0	0.0361
175	2.520	1.900	95.0	905.0	0.0434
195	2.770	2.130	107.0	893.0	0.0491
215	3.030	2.390	119.0	881.0	0.0550
235	3.290	2.640	132.0	868.0	0.0615
255	3.490	2.840	142.0	858.0	0.0665
275	3.670	3.020	151.0	849.0	0.0711
315	4.000	3.340	167.0	833.0	0.0794
345	4.440	3.780	189.0	811.0	0.0910

Note: Reaction temperature: $70 \pm 0.05^{\circ}$ C. The same conditions as TABLE I.

TABLE III

KINETIC DATA

Time (min.)	Titer (ml.)	(T-B)corr. (ml.)	$n_{(I_2)}$ (mole x 10^5)	$n_{(p\text{-DMIA})}$ (mole x 10^5)	$\log \frac{n_o}{n_o - X}$
0	0.120	0.120	6.0	994.0	0.0026
5	0.290	0.250	13.0	987.0	0.0056
10	0.650	0.580	29.0	971.0	0.0128
15	1.130	1.020	51.0	949.0	0.0227
20	1.620	1.480	74.0	926.0	0.0334
25	2.050	1.980	99.0	901.0	0.0453
30	2.540	2.340	117.0	883.0	0.0540
35	2.950	2.710	136.0	864.0	0.0635
40	3.400	3.140	157.0	843.0	0.0742
45	3.830	3.540	177.0	823.0	0.0846
55	4.550	4.200	210.0	790.0	0.1024
65	5.270	4.870	244.0	756.0	0.1215

Note: Reaction temperature: 90 ± 0.05° C. The same conditions as TABLE I.

TABLE IV

KINETIC DATA

Time (min.)	Titer (ml.)	(T-B)corr. (ml.)	$n(I_2)$ (mole x 10^5)	$n_{(p\text{-IMIA})}$ (mole x 10^5)	$\log \frac{n_o}{n_o - X}$
5	0.16	0.12	6.0	994.0	0.0026
10	0.33	0.26	13.0	987.0	0.0056
15	0.52	0.42	21.0	979.0	0.0092
20	0.73	0.59	29.0	971.0	0.0128
25	0.91	0.74	37.0	963.0	0.0164
30	1.08	0.88	44.0	956.0	0.0194
40	1.42	1.19	59.0	941.0	0.0264
50	1.82	1.50	75.0	925.0	0.0339
60	2.12	1.74	87.0	913.0	0.0395
70	2.42	2.00	100.0	900.0	0.0458
80	2.81	2.36	118.0	882.0	0.0545
90	3.15	2.66	133.0	867.0	0.0620
105	3.56	3.03	152.0	848.0	0.0716
120	3.97	3.41	172.0	828.0	0.0820
135	4.39	3.80	190.0	810.0	0.0915
150	4.74	4.13	207.0	793.0	0.1007
175	5.07	4.45	223.0	777.0	0.1096
190	5.33	4.70	240.0	760.0	0.1192

Note: Reaction temperature: $80 \pm 0.05^\circ$ C. The same conditions as TABLE I except 0.0_2 M HCl concentration.

TABLE V

KINETIC DATA

Time (min.)	Titer (ml.)	(T-B)corr. (ml.)	$n_{(I_2)}$ (mole x 10^5)	$n_{(p\text{-DMIA})}$ (mole x 10^5)	$\log \frac{n_o}{n_o - x}$
5	0.23	0.15	8.0	992.0	0.0035
10	0.43	0.30	15.0	985.0	0.0066
15	0.66	0.59	30.0	970.0	0.0132
20	0.85	0.64	32.0	968.0	0.0141
25	1.12	0.87	44.0	956.0	0.0195
30	1.43	1.15	58.0	942.0	0.0259
35	1.48	1.17	59.0	941.0	———
45	1.92	1.55	78.0	922.0	0.0353
55	2.40	1.98	84.0	916.0	0.0381
67	2.81	2.34	117.0	883.0	0.0540
75	3.26	2.75	138.0	862.0	0.0645
85	3.60	3.04	152.0	848.0	0.0716
95	3.75	3.34	167.0	833.0	0.0794
110	4.60	3.92	196.0	804.0	0.0943
125	5.02	4.27	214.0	786.0	0.1046

Note: Reaction temperature: 80 ± 0.05° C. The same conditions as TABLE I except 0.10 M HCl concentration.

TABLE VI

KINETIC DATA - DEUTERIUM EFFECT

Time (min.)	Trans.[a] (%)	$n_{(I_2)}$[b] (mole x 10^5)	$n_{(I_2)corr.}$[c] (mole x 10^5)	$n_{(p\text{-DMIA})}$ (mole x 10^5)	$\log \frac{n_o}{n_o - X}$
25	95.0	14.0	9.0	991.0	0.0039
30	94.0	18.0	12.0	988.0	0.0052
40	93.0	20.0	14.0	986.0	0.0060
50	92.0	24.0	15.0	985.0	0.0066
60	90.0	31.0	18.0	982.0	0.0079
75	87.5	40.0	22.0	978.0	0.0097
90	85.0	48.0	27.0	973.0	0.0119
105	83.5	56.0	32.0	968.0	0.0141
120	82.0	61.0	34.0	966.0	0.0150
135	80.0	68.0	39.0	961.0	0.0173
150	79.0	75.0	44.0	955.0	0.0195
165	78.0	79.0	46.0	954.0	0.0205
180	76.8	85.0	52.0	948.0	0.0232

Note: Reaction temperature: 80 ± 0.05° C. The composition of reaction mixture: 0.01 M of N, N-dimethyl-p-iodoaniline, 0.25 M KI and 0.05 M HCl.

a. Transmittance (%)

b. Converted from transmittance

c. Blank correction

II. Calculations

Kinetic Rate Constants: The graphical method is used to obtain the constants from the kinetic data. The last columns of the tables, log (n_o/n_{o-X}), are plotted against time, and the graphs, Figure 2 - 7, are obtained.

First order rate constants are obtained from the slopes of the lines obtained from the plots.

If after time t, X moles of the sample compound have reacted, the remaining concentration of the compound is n_o-X, where n_o is the initial concentration of the compound. The rate of formation of the product is dX/dt, so that

$$\frac{dx}{dt} = k\,(n_o - X)$$

By integration,

$$-\ln\,(n_o - X) = kt + \text{constant}$$

Substituting the boundary conditions,

$$\ln \frac{n_o}{n_o - X} = kt$$

is obtained. This integrated equation shows that the rate constant, k, is obtained by plotting the values of ln (n_o/n_o-X) against the reaction time.

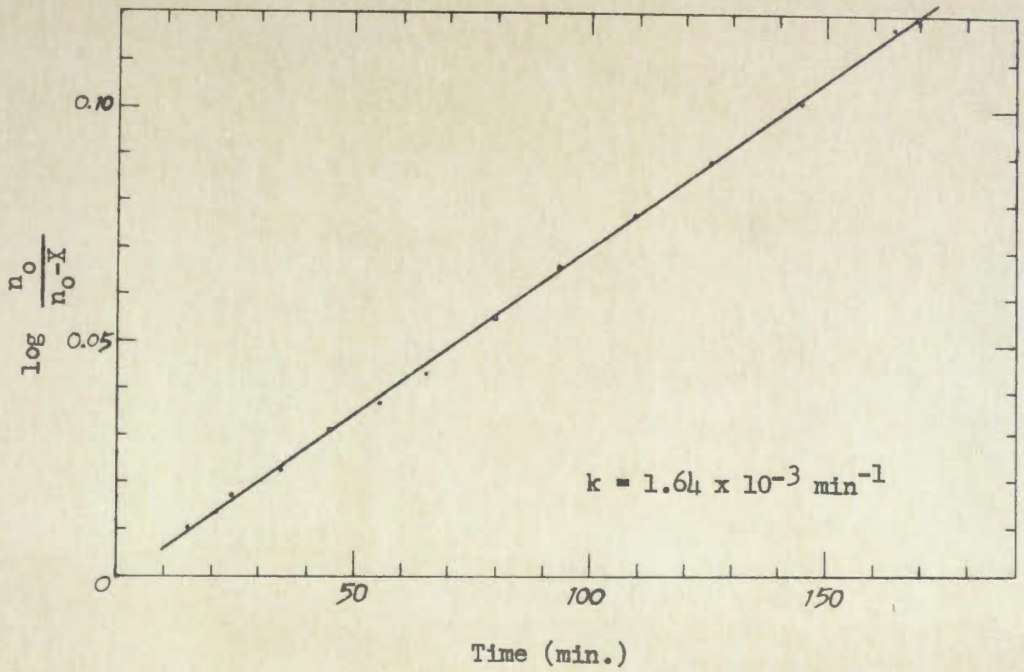


Figure 2. Plot of TABLE I

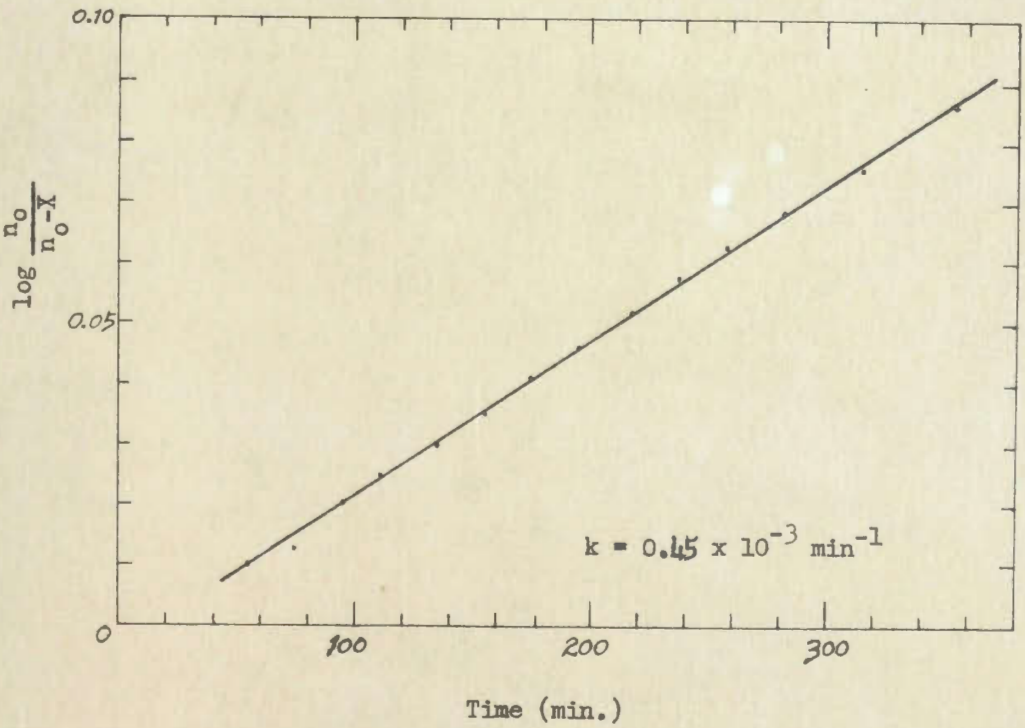


Figure 3. Plot of TABLE II

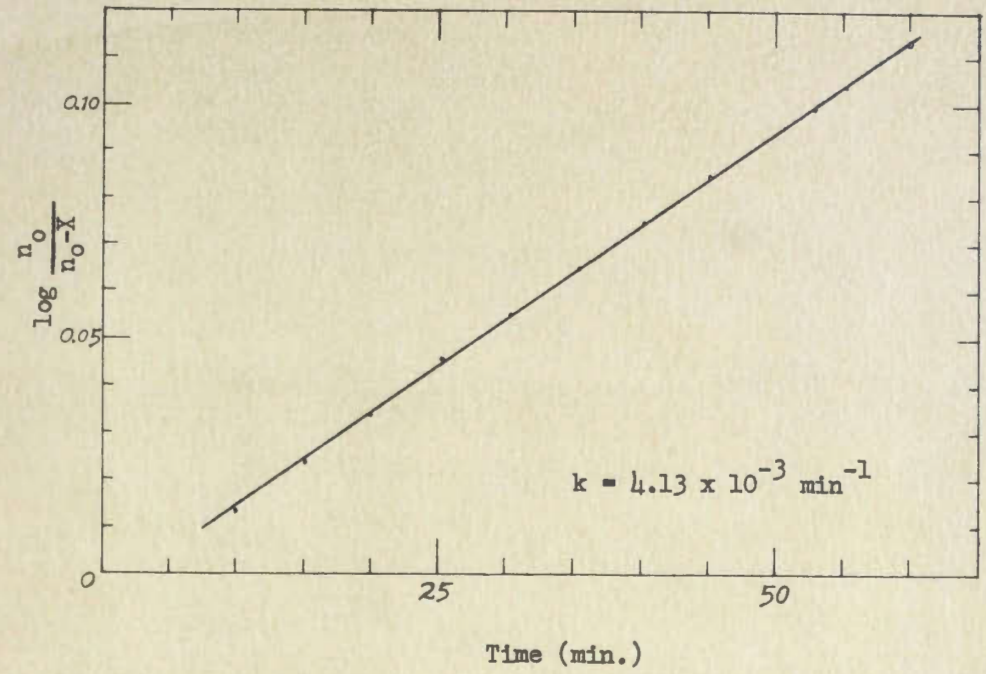


Figure 4. Plot of TABLE III

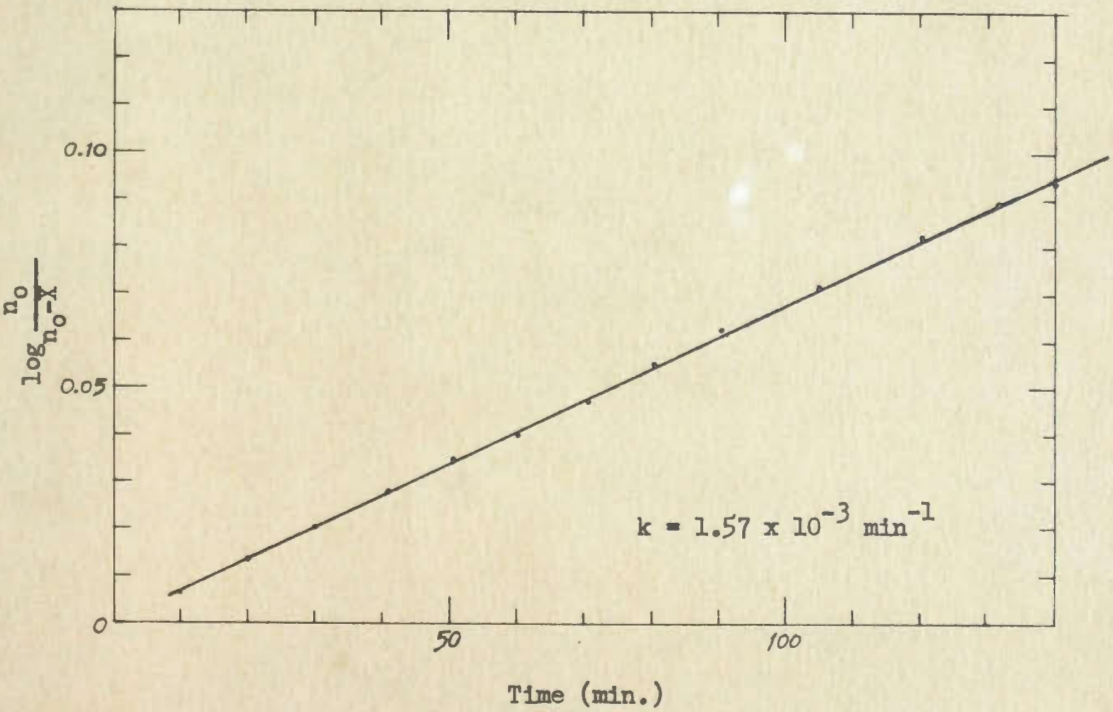


Figure 5. Plot of TABLE IV

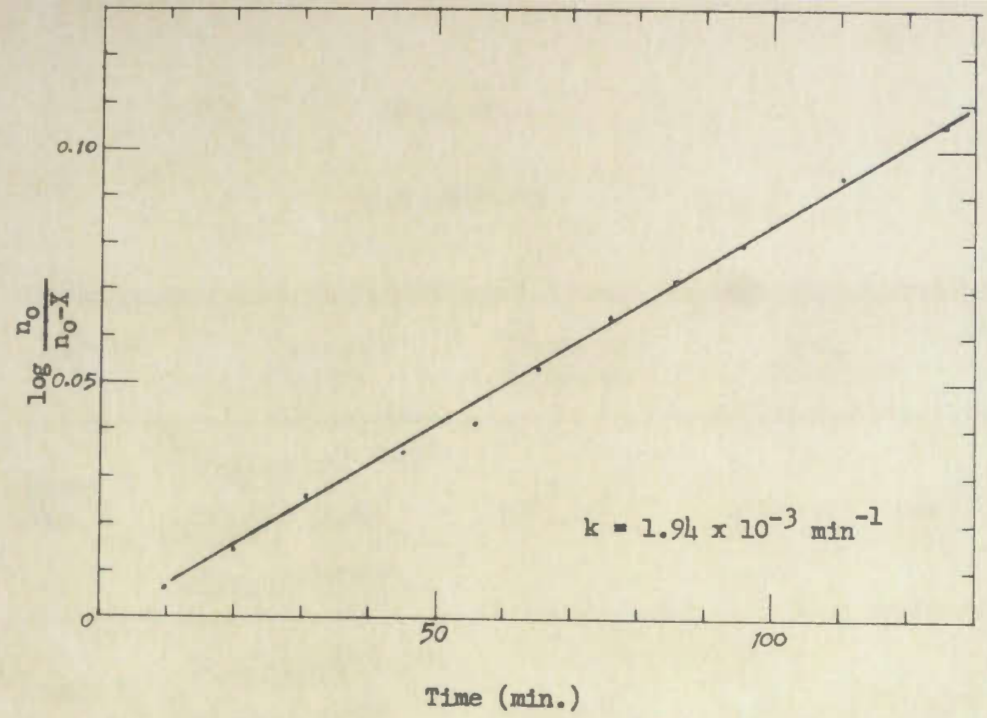


Figure 6. Plot of TABLE V

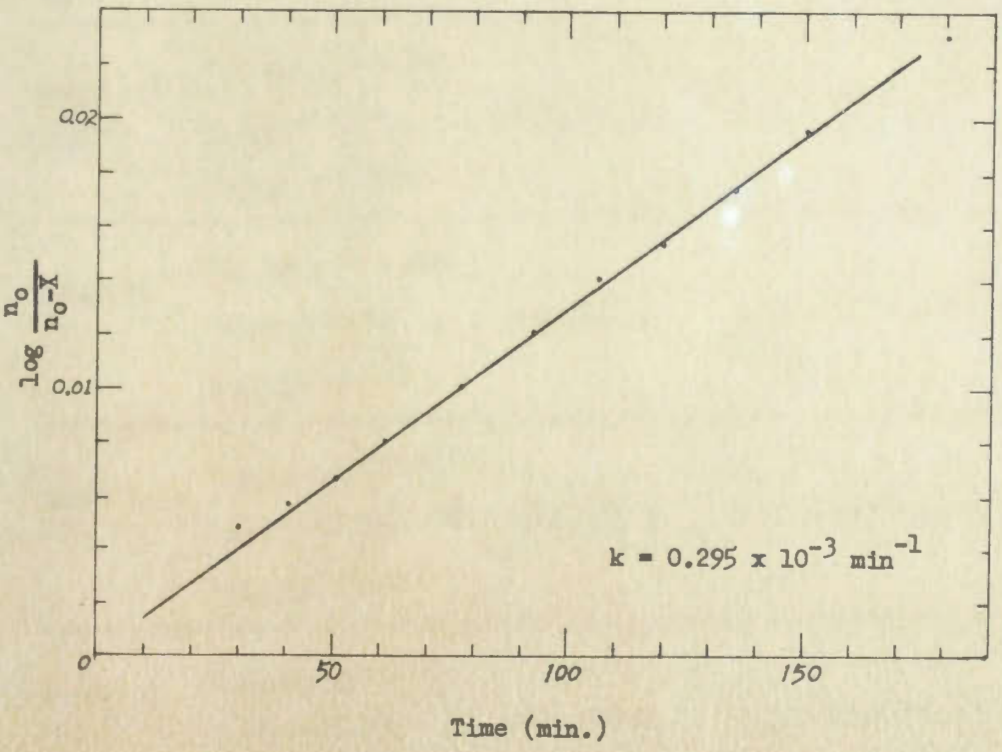


Figure 7. Plot of TABLE VI

TABLE VII

RATE CONSTANTS

Kinetic Data	Reaction Mixture	Reaction Temperature	Rate Constants
TABLE I Fig. 2	$n_{o(p\text{-}DMIA)}$= 0.1M $n_{o(KI)}$= 0.25M $n_{o(HCl)}$=0.05M	80±0.05° C	1.64×10^{-3} min^{-1}
TABLE II Fig. 3	$n_{o(p\text{-}DMIA)}$= 0.01M $n_{o(KI)}$= 0.25M $n_{o(HCl)}$= 0.05M	70±0.05° C	0.645×10^{-3} min^{-1}
TABLE III Fig. 4	$n_{o(p\text{-}DMIA)}$= 0.01M $n_{o(KI)}$= 0.25M $n_{o(HCl)}$= 0.05M	90±0.05° C	4.13×10^{-3} min^{-1}
TABLE IV Fig. 5	$n_{o(p\text{-}DMIA)}$= 0.01M $n_{o(KI)}$= 0.25M $n_{o(HCl)}$= 0.02M	80±0.05° C	1.57×10^{-3} min^{-1}
TABLE V Fig. 6	$n_{o(p\text{-}DMIA)}$=0.01M $n_{o(KI)}$= 0.25M $n_{o(HCl)}$= 0.02M	80±0.05° C	1.94×10^{-3} min^{-1}
TABLE VI Fig. 7	$n_{o(p\text{-}DMIA)}$= 0.01M $n_{o(KI)}$= 0.25M $n_{o(HCl)}$= 0.10M	80±0.05° C	0.295×10^{-3} min^{-1}

Activation Energy: The activation energy is obtained from the Arrhenius equation of activation energy,

$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2} ,$$

assuming that the activation energy is independent of the reaction temperature. From the integrated form of the above equation,

$$\ln k = - \frac{E_a}{RT} + \ln A ,$$

E_a, the activation energy, is obtained by plotting the ln k values against the corresponding value of $1/T$.

k = the rate constant at the absolute temperature, T.

A = the frequency factor.

The ln k - $1/T$ curve is shown in Fig. 8.

The Activation energy of the Deiodination of N, N-Dimethyl-p-iodoaniline = 1.095 kcal/mole

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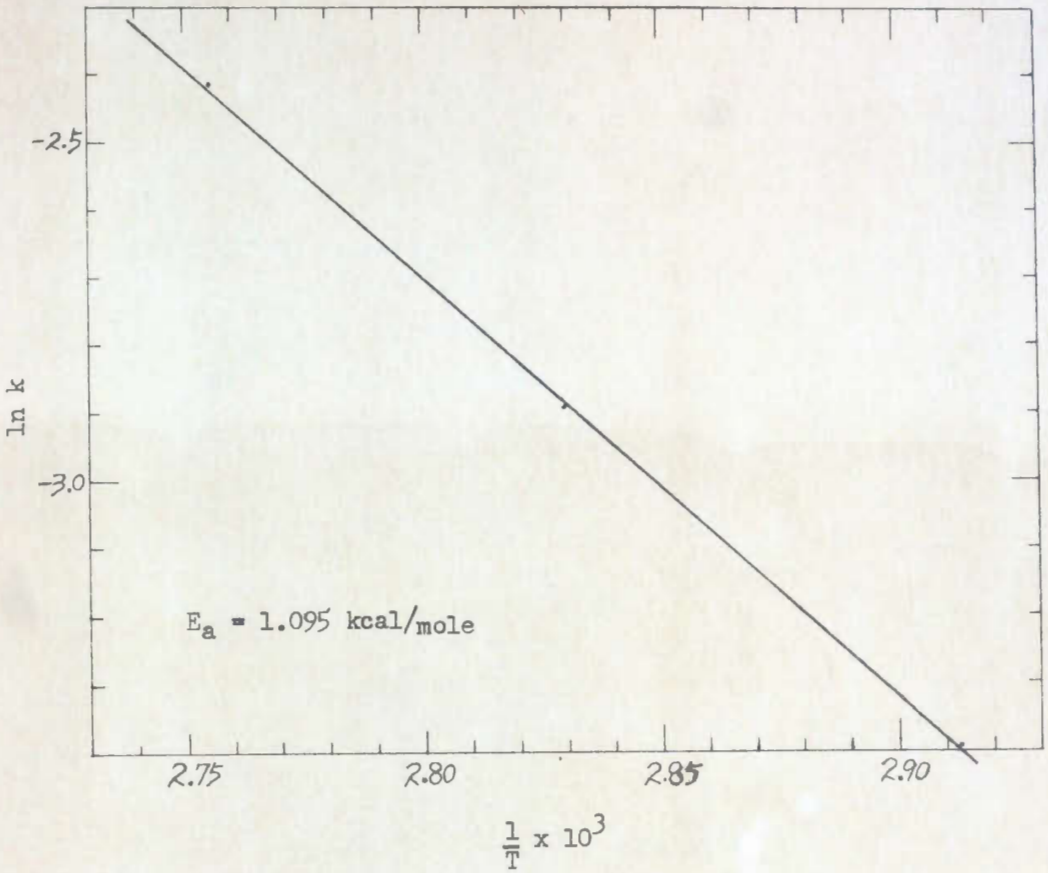


Figure 8. Temperature Dependence of Rate Constants

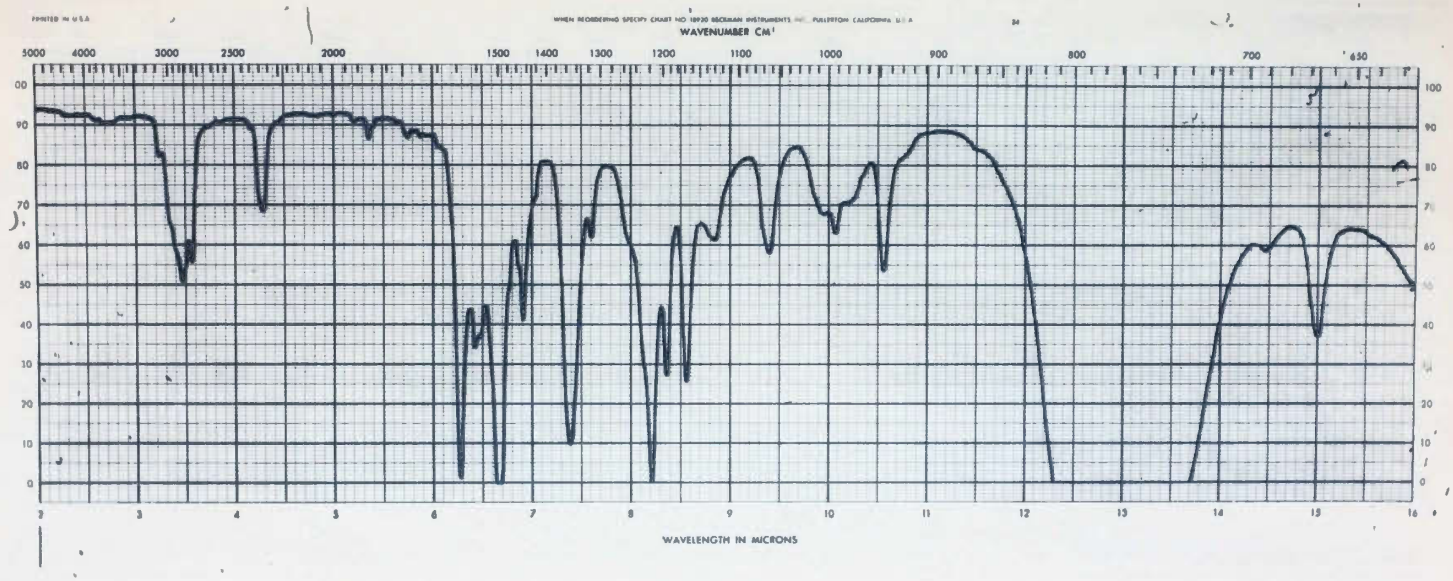


Figure 9. Infrared Absorption Spectrum of N, N-Dimethyl-p-iodoaniline with CCl_4

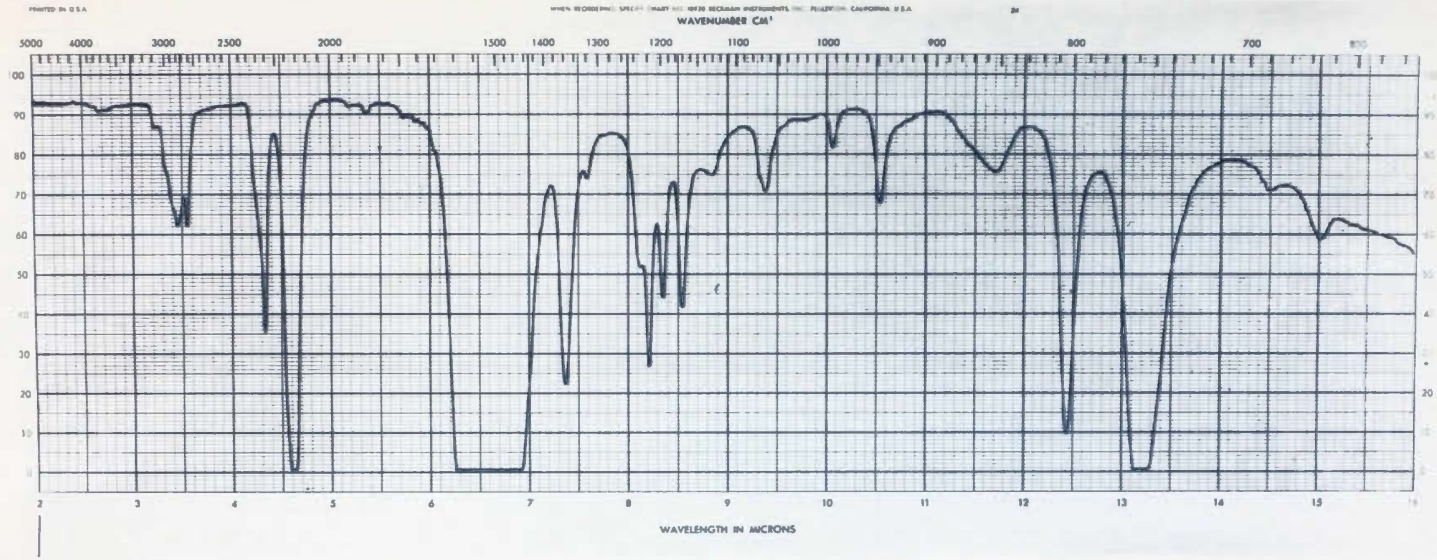


Figure 10. Infrared Absorption Spectrum of N, N-Dimethyl-p-iodoaniline with CS_2

DISCUSSIONS

I. The Reaction Order

Extending the mechanism of protodeiodination to the case of the N, N-dimethyl-p-iodoaniline, it was anticipated that the reaction follows a S_E2 mechanism, with the decomposition of the activated complex as the rate determining step.

The consequence of the present research confirmed that this anticipation was correct and that the order of the total reaction was first order with respect to the concentration of N, N-dimethyl-p-iodoaniline in the system.

The kinetic measurement could not be extended beyond about 25% progress of the reaction because of the experimental difficulty, but the initial stage of reaction was considered to be significant in the kinetic investigation.

The kinetic expression of the reaction was as follows:

$$-\frac{d[T]}{dt} = -\frac{d[n]}{dt} = \frac{d[I_3^-]}{dt} = k[n]$$

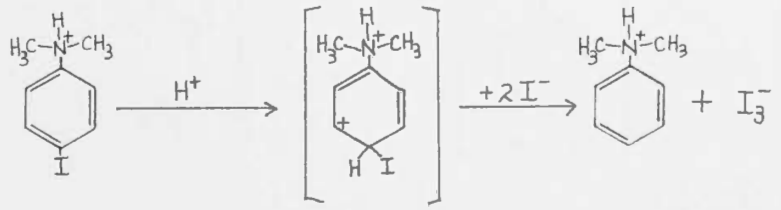
$[T]$: The concentration of the activated complex

$[n]$: The concentration of N, N-dimethyl-p-iodoaniline

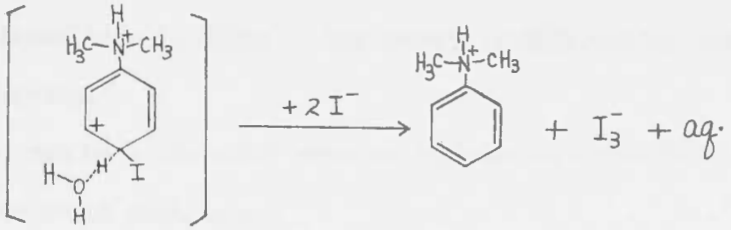
$[I_3^-]$: The concentration of triiodide ion

II. The Mechanism of Deiodination

Present research showed that the S_E2 mechanism could be extended to the case of N, N-dimethyl-p-iodoaniline.



As discussed earlier in this report, the activated complex decomposition process included a proton transfer from an associated hydronium ion to the molecule of N, N-dimethyl-p-iodoaniline.

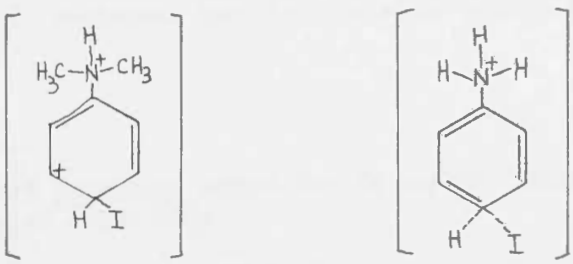


The decomposition process involved the following problems; (1) the time order of proton transfer and C - I bond breaking, (2) the rate determining step, (3) relative significance of (1), and (2), and (4) solvent effect.

These problems cannot be discussed conclusively without further evidence. However, the deuterium effect showed that the proton transfer is significant. The replacement of solvent H_2O by D_2O decreased the deiodination rate by a factor of about 6.

III. The Stability of the Activated Complex

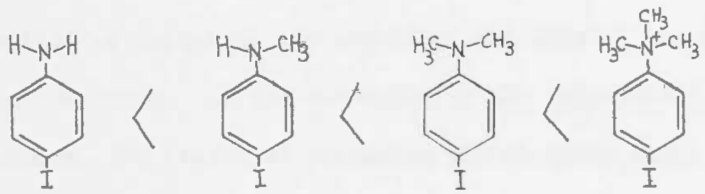
The activation energy of the deiodination of N, N-dimethyl-p-iodoaniline was found to be 7.7 kcal/mole. This value is considerably smaller than the value for the case of p-iodoaniline (36.2 kcal/mole). This difference indicated that the activated complex of N, N-dimethyl-p-iodoaniline is more unstable than that of p-iodoaniline in acidic media.



The stability of the activated complex also depends upon the stability of the products and reactants. However, the statement that the activated complex of N, N-dimethyl-p-iodoaniline decomposes faster can be rationalized in terms of the strong meta directing effect of $-\overset{+}{N}H(CH_3)_2$ group.

There can be a few other ways to explain this situation, but all of them are still ambiguous.

The replacement of $-\overset{+}{N}H_3$ group by $-\overset{+}{N}HMe_2$ increased the rate of deiodination by a factor of 5 at 80°C. This factor is the ratio of rate constants of that temperature. The factor of 5 is due to the replacement of two hydrogens of amine by two methyl groups. Consequently we can arrive at the following sequence, if we agree with the above reasoning.



	I	II	III	IV
factor	1	2.5*	5	7.5*

IV. Deuterium Effect

The ratio, k_{H2O} / k_{D2O}, of 5.6 was calculated by comparing the rate constants of deiodination in H_2O medium and D_2O medium at 80°C. The ratio, 5.6, indicates that the deuterium effect is remarkable in this case.

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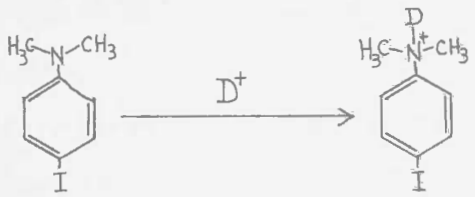
*These are predicted values for II and IV, relative to experimental values of I and III.

As discussed earlier in this report, the deuterium effect indicates that the proton transfer is significant in the rate determining step. This factor, 5.6, is about the same as the value, 5.8, of the case of p-iodoaniline.[2]

The deuterium effect, particularly in the case of N, N-dimethyl-p-iodoaniline, is complicated by the fact that N, N-dimethyl-p-iodoaniline in acidic deuterium oxide exists as N-deutero-N, N-dimethyl-p-iodoanilinium ion.



Therefore, the observed deuterium effect is a result not only of the lagging effect of deuterium ion transfer, but also of the effect of substituted deuterium. If the deuterium of the amine could be replaced by a proton, the factor of deuterium effect would vary. The significance of the effect of the deuterium on the amine requires further evidence.

V. Iodine - addition Complex

The reaction mixture of the title reaction consisting of N, N-dimethyl-p-iodoaniline, acid and molecular iodine has a strong tendency toward complex formation. The composition of the complex varies, depending upon the concentrations of N, N-dimethyl-p-iodoaniline and iodine. Those iodine-addition complexes are stable in strong acidic solution and at temperatures below room temperature, and decompose upon addition of thiosulfate solution.

A note by Dimroth and Leimbach[5] gives a short description of some complexes. However, the author believes that further research is necessary to characterize this complicated iodine-complex formation.

SUMMARY

A kinetic investigation has been made to give evidence of a proposed mechanism of protodeiodination of N, N-dimethyl-p-iodoaniline. The present research showed that the proposed S_E2 mechanism could be applied to the deiodination of N, N-dimethyl-p-iodoaniline. The reaction proceeded faster by a factor of 5 than the deiodination of p-iodoaniline.

The stability of the activated complex was discussed in terms of activation energy, which was obtained from the rate constants at three different temperatures. The activation energy of the title reaction was found to be 1.1 $kcal/_{mole}$. This value was compared with the value, 36.2 $kcal/_{mole}$, for p-iodoaniline.

A comparison of the results of the present research with that of the deiodination of p-iodoaniline led us to a sequence of different iodoanilines in order of their reactivity toward deiodination in acid medium.

The kinetic deuterium effect on the rate of reaction was determined. The ratio, k_{H_2O}/k_{D_2O} at 80°C, was 5.8, which was comparable to the deuterium effect of p-iodoaniline (5.6). This value indicated that proton transfer is the significant step in the iodine-scission process.

Infrared spectra of N, N-dimethyl-p-iodoaniline with CCl_4 and CS_2 as solvents were obtained. The expectation that the absorption peak of C - I bond of N, N-dimethyl-p-iodoaniline is shifted toward lower energy side than that of p-iodoaniline could not be observed

because the absorption range of C - I bond was out of the limited range of the available infrared spectrophotometer (Beckman - IR5A).

A strong tendency of the reaction mixture to form iodine-addition complexes has been noticed and described.

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